

Microscopic model for spreading of a two-dimensional monolayer

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We study the behavior of a monolayer, which occupies initially a bounded region on an ideal crystalline surface and then evolves in time due to random hopping of the monolayer particles. In the case when the initially occupied region is the half-plane $X \leq 0$, we determine explicitly, in terms of an analytically solvable mean-field-type approximation, the mean displacement $X(t)$ of the monolayer edge. We find that $X(t) \approx A\sqrt{D_0 t}$, in which law D_0 denotes the bare diffusion coefficient and the prefactor A is a function of the temperature and of the particle-particle interactions parameters. We show that A can be greater, equal or less than zero, and specify the critical parameter which distinguishes between the regimes of spreading ($A > 0$), partial wetting ($A = 0$) and dewetting ($A < 0$).

1 Introduction

It has been well appreciated since the pioneering work by Hardy [1] that a liquid droplet spreading on a solid, although it undergoes no visible change in shape, emits a very thin invisible film - the precursor, which advances at a seemingly faster rate than the nominal contact line. Hardy was able to detect its presence by observing a significant change in the value of the static friction of the surface. Stating that he was unable to conceive of a mechanism by which the film can be emitted and spread further along the solid substrate, Hardy proposed that spreading of the film occurs by a process involving a continual condensation of vapor. Bangham and Saweris [2] have demonstrated, however, that such a film shows up even in the absence of any vapor fraction, suggesting thus that the physical mechanism giving rise to the precursor film can be different from the evaporation/condensation scheme. Later, using ellipsometric and interferometric techniques, Bascom et al. [3] investigated the spreading of the precursor film from a more quantitative point of view. They examined the behavior of various non-polar liquids on clean metal surfaces in the presence of both saturated and unsaturated air and concluded that the precursor film is always present; making the air saturated or unsaturated with vapor, roughening the surface and purifying the liquids does not eliminate the film, but only affects the speed at which it spreads over the solid. The thickness of the film was also found to depend essentially on the liquid/solid system under study; it can be as small as molecular size (several angstroms) or can

amount to hundreds of angstroms (see [4] for a review). Particularly, the droplet of squalane spreading on stainless steel exhibited a precursor with a thickness of approximately 20 angstroms.

Spreading rates and dynamical shapes of advancing precursor films have been studied thoroughly for many years, both experimentally and theoretically (see [3, 4, 5, 6, 7, 8] and references therein). These studies have resulted in a rather good understanding of the problem. It was realized that the precursor film appears not because of the condensation of the vapour fraction, which process may, of course, exist but plays a minor role. Rather, such a film extracts from the droplet and advances along the solid surface due to the presence of attractive interactions between the fluid molecules and the solid atoms [3, 4, 5, 6, 7, 8]. Later, it even became possible to elaborate consistent hydrodynamic theory of spreading of thin precursor films, based on the celebrated lubrication approximation of fluid mechanics [4, 5, 6, 9]. In particular, this considerable theoretical advancement allowed to resolve an old-standing enigma concerning the dynamics of the nominal contact line: it was well documented experimentally (see, e.g. [5] and references therein) that in the complete spreading regime the radius R of the nominal contact line shows a slow growth with time, $R \sim t^{1/10}$, where the exponent $1/10$ is universal, i.e. dependent only on the geometry and independent of the precise nature of the liquid/solid system. As a matter of fact, in this law even the prefactor appears to be insensitive to the spreading power S , which is the characteristic of a given liquid/solid system and equals the difference of the surface tensions of the solid-vapour, solid-liquid and liquid-vapour interfaces respectively. On the other hand, conventional analysis, which considers the gradient of the liquid/solid free energy as the driving force of spreading, predicts much faster growth which is, moreover, dependent on the spreading power. The hydrodynamic picture developed in [5, 9] has found the solution of this controversy, showing that the spreading power S is totally dissipated into the precursor film, such that the dynamics of the nominal contact line is actually not affected by S . Besides, it has been recognized that contrary to the general belief, the final state in complete ($S \geq 0$) spreading of a liquid droplet is not necessarily a monolayer covering the solid surface: it is only the macroscopic part of the droplet which spreads completely; the precursor film, however, can cease to spread further after the macroscopic part of the droplet is exhausted and form a stable, nearly planar droplet-like structure - the so-called "pancake" [5, 9, 10, 11, 12]. The thickness of the pancake is fixed by a competition between S and long-range attractive interactions with the substrate, which tend to thicken the film. For pure van der Waals interactions the thickness $e_p(S)$ of the pancake is $e_p(S) \approx a(3\gamma/2S)^{1/2}$, where a is the molecular size and γ is the macroscopic surface tension of the liquid. In general, $\gamma/S \sim 1$ and $e_p(S) \sim a$, but if S is small, $e_p(S)$ can be relatively large. Therefore, within the framework of the hydrodynamical approach it is the pancake thickness $e_p(S)$ which sets the upper bound on the thickness of the precursor film. Details concerning different "pancake" structures and their experimental observations can be found in a recent review [13].

1.1 Experimental studies of spreading of molecularly thin films.

Hydrodynamic approach, however, presumes a certain lower cut-off length comparable to the molecular size, below which it is not justified. With the advent of modern experimental techniques, capable of studying behavior of precursor films whose thickness is in the molecular range, it has become clear that the developed theoretical concepts concerning the dynamics and equilibrium properties of thin wetting films can only apply to sufficiently thick films. In fact, for molecular films significant departures from the hydrodynamic picture have been observed experimentally [14, 15, 16, 17, 18].

Extensive ellipsometric measurements [14, 15, 16, 17, 18] have elucidated several remarkable features, which seem to be quite generic for spreading molecularly thin films:

(i) Experimental measurements carried out on different substrates and with different types of simple liquids, polymeric and surfactant melts, showed unambiguously that the radius of the precursor film grows with time t as $t^{1/2}$. The exponent $1/2$ appears to be completely independent of the nature of the species involved. The latter affects the spreading rate only through the prefactor in the \sqrt{t} -law. Essentially the same behavior has been discovered in the capillary rise geometry, in which a vertical solid wall is put into contact with a bath of liquid. The length of the molecularly thin film extracting from meniscus and climbing upwards along the wall was also shown to grow in proportion to the square-root of time [17]. This shows that the \sqrt{t} -law is seemingly independent of the precise curvature of the film's edge, which is a circular line in case of the sessile drops and planar in the capillary rise geometries.

(ii) It was found that the particle density along the film is not necessarily constant. In several experimental situations, particularly, for the droplets of squalane, the radial density was seen to vary strongly with the distance from the nominal contact line and the variation was progressively more pronounced for larger spreading rates.

(iii) For intermediate-energy substrates a fascinating transient regime of "terraced spreading" was discovered [14, 15], in which several molecularly thin precursor films extract from the macroscopic droplet and spread on top of one another each one growing as \sqrt{t} . Such a regime may last within a considerably long period of time, until the layers on the top run out and one eventually ends up with a bounded monolayer on the solid surface. Depending on the physical conditions, the monolayer may then either continue to spread with the radius growing in proportion to \sqrt{t} , (but with a different prefactor, of course), or may remain in form of a wetted spot [17]. The remarkable "terraced wetting" effect has been also seen in the capillary rise geometries. Besides, recent numerical, Molecular Dynamics simulations of liquid drop spreading were able to reproduce both the "terraced" wetting spreading regime and the \sqrt{t} -law (see [29, 30, 31] and references therein).

1.2 Theoretical studies of spreading of molecularly thin films.

Theoretical analysis of the physical mechanisms underlying the seemingly universal \sqrt{t} -law and the "terraced wetting" phenomenon followed three different lines of thought:

In [19] an analytical description of the "terraced wetting" phenomenon has been proposed, in which the liquid drop on a solid surface was considered as a completely layered structure, each layer being a two-dimensional (2D) incompressible fluid of molecular thickness but with a macroscopic radial extension. The interaction energy of a molecule in the n th layer with the solid substrate was taken in the general form as a negative, decreasing function of the distance from the substrate. Next, it was supposed that spreading proceeds by filling the successive layers by the molecules from the above layers, which process is favored by the attractive interactions with the solid. In each layer there is a horizontal, radial particle current and vertical permeation fluxes, one from the upper layer and one towards the lower layer, which appear to be located in a very thin "permeation ribbon" just at the droplet surface - the core of the droplet seems to be a "stagnant" liquid with respect to the vertical mass transfer. In such an approach, de Gennes and Cazabat [19] have found that whenever the distinct layers grow at a comparable rate, they grow in proportion to $t^{1/2}$. In case when the precursor film grows at a much faster rate than all other layers, the model predicts that the precursor grows in proportion to $(t/\ln(t))^{1/2}$. Apart from the theoretical prediction of the \sqrt{t} -law, the model allows to

draw certain conclusions concerning the appearance of the "terraced wetting" regime. To some extent, the underlying assumptions and predictions of this model concerning the intermediate time behavior were confirmed by Molecular Dynamics simulations [20].

An alternative description within the framework of non-equilibrium statistical mechanics has been elaborated in [21, 22, 23]. Here, an interfacial model for the non-volatile fluid edge has been developed and analysed in terms of Langevin dynamics for the displacements of horizontal solid-on-solid (SOS) strings $\{h_j\}$ at increasing heights $j = 1, \dots, L$ from the substrate, which strings have essentially the same meaning as the layers in the de Gennes-Cazabat model [19]; h_j can be thought of as the radius of the j th layer. Anticipating the discussion of results obtained in the present paper, we will describe this promising theoretical approach giving some more details. In the model developed in [21, 22, 23] the energy $U(\{h_j\})$ of a given configuration $\{h_j\}$ was described by

$$U(h_0, h_1, \dots, h_L) = \sum_{j=1}^L P(h_j - h_{j-1}) - \mu_0 h_0, \quad (1)$$

where h_0 is the length of the "precursor" film, μ_0 is the wall tension and the function $P(h_j - h_{j-1})$ determines the contribution due to the surface energy. Explicitly, it was taken as

$$P(h_j - h_{j-1}) = J \sqrt{1 + (h_j - h_{j-1})^2}, \quad (2)$$

where the parameter J is related to the surface tension; thus, the spreading power S for such a model is given by $S = \mu_0 - J$. In the limit $h_j - h_{j-1} \ll 1$, the function in Eq.(2) reduces to the standard Gaussian form, i.e.,

$$P(h_j - h_{j-1}) \approx J (h_j - h_{j-1})^2, \quad (3)$$

while for $|h_j - h_{j-1}| \gg 1$ it obeys

$$P(h_j - h_{j-1}) \approx J |h_j - h_{j-1}| \quad (4)$$

In other words, Eq.(2), which bears a certain relationship with the Lifschitz equation describing the time evolution of an interface due to the effects of the surface tension [24], supposes the following, quite realistic behavior of the interfacial energy: for small distortions of the interface the surface energy is Gaussian, while the cost of a large distortion is linear with the distortion size. Dynamics of the strings $\{h_j\}$ is then described by the set of L coupled Langevin equations

$$\xi \frac{\partial h_k}{\partial t} = - \frac{\partial U(\{h_j\})}{\partial h_k} + f(h_k; t), \quad (5)$$

where ξ denotes the friction coefficient, which is supposed to be the same for all layers, and $f(h_k; t)$ is Gaussian, delta-correlated noise. The model in Eqs.(1),(2) and (5) allows for an analytical, although rather complicated solution, which shows an extraction of the precursor film and "terraced" forms of the dynamical thickness profiles. It predicts that for $\mu_0 > J$, ($S > 0$), and for sufficiently short precursors, (such that the dominant contribution to the surface energy is given by Eq.(3)), the length of the film increases with time as

$$h_0(t) \sim \sqrt{(\mu_0 - J) t}, \quad (6)$$

which resembles the experimentally observed behavior. For sufficiently large precursor, for which the energy increases linearly with the length, Eq.(4), the layer on top of substrate is found to show a faster growth

$$h_0(t) \sim (\mu_0 - J) t \quad (7)$$

Finally, it was found that exactly at the wetting transition point $\mu_0 = J$, the precursor film advances in proportion to

$$h_0(t) \sim \sqrt{t \ln(t)} \quad (8)$$

Consequently, this model predicts that at very large times the advancing precursor film attains a constant velocity; the \sqrt{t} -law is thus found only as a transient stage. Besides, dynamics of the layers at large distances from the substrate and, respectively, of the macroscopical dynamical contact angle disagree with experimental data. Apparently, this inconsistency with experiments can be traced back to the fact that focusing on the evolution of the interface only, the model neglects dynamics in the liquid phase and thus discards the energy losses due to viscous flow pattern, generated in the spreading droplet. In [21, 22, 23] a viscous-type dissipation is assumed with constant friction coefficient, which represents rather generic and oftenly loose assumption used in the descriptions of the phase-separating boundary dynamics in terms of the time-dependent Landau-Ginzburg-type model. In fact, the model underestimates the dissipation in each layer h_j . Account of the energy losses in viscous flows in the core region of the droplet and of the dissipation in the vicinity of the solid substrate actually results in the overall viscous-type dissipation, which is not surprising for the system with many degrees of freedom. The friction coefficient, however, turns out to be weakly dependent on the height above the substrate and, what is essentially more important, appears to be an increasing function of h_j . Therefore, these dissipation channels should be certainly taken into account within the framework of the powerful theoretical approach proposed in [21, 22, 23], which may result in a consistent dynamical theory of partial and complete wetting valid for all scales. Such improvements are currently under investigation [25].

Lastly, a microscopic dynamical model for spreading molecularly thin films has been devised in [26, 27]. Here the film was considered as a two-dimensional hard-sphere fluid with particle-exchange dynamics. Attractive interactions between the particles in the precursor film were not ostensibly included into the model, but introduced in a mean-field-type way - it was supposed that the film is enclosed by the SOS-model interface, in which the parameter J was treated as some (not specified in [26, 27]) function of the amplitude of the particle-particle attractions. The film was assumed to be connected to a reservoir of infinite capacity - the macroscopic drop. The rate at which the reservoir may add particles into the film was related to the local particle density in the film in the vicinity of the nominal contact line and to the strength of the van der Waals attractive interactions between the fluid particles and solid atoms within the framework of the standard Langmuir adsorption theory. Contrary to [19] and to the hydrodynamic picture of [5], the model in [26, 27] emphasized the issues of compressibility and molecular diffusion at the expense of the hydrodynamic flows; it was assumed that the reservoir and the film are in equilibrium with each other, so that there is no flow of particles from the reservoir which pushes particles to move along the substrate away of the droplet. In this approach, the \sqrt{t} -law for growth of the film was first analytically obtained for the capillary rise geometries and it was actually found that the density in the film does varies strongly with the distance from the reservoir. This agrees, at least qualitatively, with experimental observations (see the Introduction, 1.1, (ii)), but no direct comparison was made, as yet. Clearly, the factor which makes such a comparison quite awkward is that the spreading rate is expressed through the parameter J , which is supposed to be some known parameter. As it will be made clear below, this parameter depends on the particle-particle attractions and moreover, on the density distribution in the precursor film. Further on, the critical conditions under which spreading of the precursor film may take place were established in [26, 27]. It was also suggested that the physical mechanism underlying the \sqrt{t} -law stems from diffusive-type transport of vacancies from the edge of the advancing film to the macroscopic liquid edge, where they perturb the equilibrium between the macroscopic drop and the film and get filled with fluid particles from the macroscopic liquid drop. In [28] this picture was extended to the case of sessile drops and

it was shown analytically that the curvature corrections result only in a weak slowing down of the precursor spreading; the film radius grows in this case as $(t/\ln(t))^{1/2}$, which prediction agrees with [19].

To close this introductory part of our paper we mention several analytical studies of the process, which can be thought of as the reverse counterpart of wetting, - dewetting of microscopically thin liquid films from solid substrates. Recently Ausserré et al. [32] investigated analytically dewetting of a monolayer, which was assumed to proceed by nucleation of holes (bare regions) and creation of "towers" - two-layer regions. Considering the monolayer as an incompressible 2D liquid, it was shown that the hole radius R (or the radius of a "tower") grows with time in proportion to $(t/\ln(t))^{1/2}$. This means that in the monolayer regime the dewetting process proceeds essentially slower than in the case of mesoscopically or macroscopically thick films, for which the behavior $R \sim t$ is generic [33, 34, 35, 36]. Another interesting example of a (forced) dewetting of a monolayer was discussed in [37] and concerned with the squeezing of a molecularly thin liquid film out of a narrow gap between two immobile solids. In [37] the mechanism responsible for squeezing was attributed to the process of spontaneous opening of holes in liquid layers; the holes are subsequently get filled by deforming solid material exerting pressure on the hole boundaries. Viewing solids as isotropic, structureless elastic media and the liquid phase in a lubricated contact between two solids as a sequence of layers, each layer being an incompressible 2D liquid, Persson and Tosatti [37] were able to estimate the critical radius of the hole, necessary to initiate further squeezing, and to define the rate of the removal process after the nucleation of a critical hole has occurred. It was shown that the radius of the hole, which exceeds initially the critical value, grows in time again in proportion to $(t/\ln(t))^{1/2}$.

2 The objectives and a brief outline of the paper.

In this paper we study analytically, in terms of a stochastic microscopic model, the behavior of a liquid monolayer in a situation, in which a monolayer occupies initially only some part of solid surface - the half-plane $X \leq 0$, Fig.1, and then is allowed to evolve in time due to the thermally activated random motion of the monolayer particles. Here we aim to calculate the time dependence of the mean displacement of the monolayer edge, defined as the position of the rightmost monolayer particles (Fig.1), to determine the prefactor in this dependence in terms of the interaction parameters and the edge tension of the monolayer.

We note that the model to be considered here clearly shares common features with many dewetting and wetting experimental situations and models, which were described in the Introduction. A monolayer in such a non-equilibrium configuration appears, for instance, at the late stages of spreading, when the liquid drop feeding the precursor film gets exhausted or in the situation when the monolayer on the solid surface is perturbed by a sudden removal of some amount of particles or by nucleation of a dewetted region - a circular hole or a patch. Such a model applies, after some minor modifications, to the dynamics of ultrathin liquid columns in nanopores or in narrow slits between solid surfaces (Fig.2). It can also serve as a microscopic description of the process of Ostwald ripening of voids, spinodal decomposition or island formation in two-dimensional adlayers. We note also that in view of the above-mentioned results concerning spreading dynamics, we expect that the precise geometry of the two-phase region is not very important; the difference between the case when the front of the monolayer is planar, as we consider here, and the case when it is a circular closed line, what should be for circular dewetted holes, can be only in the appearance of logarithmic in time corrections to the \sqrt{t} -law, important at times when the displacement of the edge becomes comparable to the radius of

the edge curvature. An important point is that both the region occupied by the monolayer and the initially dewetted region should be macroscopically large.

As opposed to [19], [32] and [37], we will regard the monolayer as an essentially discrete, molecular liquid composed of interacting particles moving randomly on an ideal crystalline surface. Particles migration is assumed to be activated by the solid atoms vibrations and will be described using the standard Kawasaki picture for particles exchange dynamics under long-range particle-particle interactions. The picture we make use thus follows closely the model elaborated in [26, 27], being different from the latter in two important aspects: first, the long-range attractive interactions between the liquid particles are here explicitly included into the dynamics, and, consequently, our results will be expressed in terms of the interaction parameters. Second, the reservoir of particles is absent, which allows us to study within a unified approach dynamics of both spreading and dewetting processes. We also hasten to remark that with regard to other dynamical wetting theories, this model is related to the Molecular Kinetic theory of wetting dynamics, proposed and developed by Blake et al. [38, 39, 40]. In this theory, which emphasizes the dissipation in the vicinity of the nominal contact line at expense of the dissipation due to viscous flows in the "bulk" droplet, the analysis of dynamics of spreading liquid droplet was reduced to a mean-field-type consideration of the forced, thermally activated motion of fluid particles which appear directly at the droplet edge. In our case, however, the driving force is not assumed *a priori*, but is found consistently as the result of the cooperative behavior, associated with the interplay between the long-range attractive particle-particle interactions and repulsion at shorter scales. As well, we deal here with simultaneous random motion of all particles in the film, not reducing the problem to consider the dynamics of only particles at the edge.

Next, we will make several simplifications, compared to real physical systems. In what follows we will assume that creation of "towers" and particles evaporation in the direction normal to the solid surface are completely suppressed by the liquid-solid attraction, and hence we will constrain our consideration to the system which always remains in a two-dimensional world. Shortcomings of this picture will be discussed below. These simplifications will permit us to focus exclusively on the dynamical processes which take place in two-dimensions and thus to single out the behavior which stems from the interplay between the compressibility and the intermolecular interactions. We note also that these mechanisms are entirely complementary to those discussed in [19, 32, 37] and, consequently, understanding of their impact on the monolayer evolution is necessary for a complete picture of the phenomenon. We remark also that such an assumption can be clearly relaxed for liquids in confined geometries, e.g. in nanopores or in narrow slits between solids, where the geometry itself rules out an appearance of the vapour phase and thickening of liquid films (Fig.2). Here we will focus, however, solely on the situation with a monolayer on top of open solid surface; relevant cases, as depicted in Fig.2, will be discussed elsewhere.

The paper is outlined as follows: In section 3 we describe the model and write down basic equations. In section 4 we discuss an approximate approach to the solution of dynamical equations. Section 5 presents the results. Finally, in section 6 we conclude with a brief summary of our results and discussion.

3 The model and basic equations.

We proceed further with more precise definitions related to the model to be studied here (see also [26, 27] for a detailed discussion). Particles of the monolayer experience two types of interactions; interactions with the solid atoms (SP) and mutual interactions with each other (PP). The SP interactions are characterized by a repulsion at short scales and a weak attraction at longer distances. The

SP repulsion keeps the monolayer particles at some short distance apart from the surface, while the attractive part of the SP potential hinders particles desorption. Following [26, 27] we assume here that the SP interactions correspond to the limit of the intermediate localized adsorption [41, 42]: the monolayer particles are neither completely fixed in the potential wells created by the SP interactions (Fig.1), nor completely mobile. Potential wells are very deep with respect to desorption (desorption barrier $U_d \gg kT$) so that only a monolayer can exist, but have a much lower energy barrier V_l against the lateral movement across the surface, $U_d \gg V_l > kT$. In this regime an adsorbed particle spends a considerable part of its time at the bottom of a potential well and jumps sometimes, due to the thermal activation, from one potential minimum to another. Thus, on a macroscopic time scale the particles do not possess any velocity.

We note that such a type of random motion is essentially different of the standard hydrodynamic picture of particles random motion in the two-dimensional "bulk" liquid phase, e.g., in free-standing liquid films, in which case there is a velocity distribution and spatially random motion results from the mutual particle-particle interactions; in this case the dynamics can be only approximately considered as an activated hopping of particles, confined to some effective cells by the potential field of their neighbors, between a lattice-like structure of such cells (see, e.g. [43, 44]). In contrast to the dynamical model to be studied here, standard two-dimensional hydrodynamics presumes that the particles do not interact with the underlying solid. In realistic systems, of course, both the particle-particle scattering and scattering by the potential wells due to the interactions with the host solid, as well as the corresponding dissipation, are crucially important [45, 46]; the latter, particularly, remove the infrared divergencies in the dynamic density correlation functions and thus make the transport coefficients finite [47, 48]. Complete dynamical description of particles migration on the solid surface can be approached apparently along the lines proposed in [47, 48] or, on a microscopic level, in terms of the cellular automaton-type description of [49]; here we will be thus concerned only with a certain approximate model of particles dynamics, appropriate for situations in which the particle-particle interactions are essentially weaker than the particle-solid interactions. We note that such an assumption actually makes sense since the latter are usually at least ten times greater than the PP interactions, and therefore should not be appreciably affected by the lateral interactions of adsorbed particles.

Turning next to the particle-particle interactions, we suppose that these are additive and central, i.e. the interaction potential $U(\vec{r}_j, \vec{r}_i)$ depends only on the distance $r = |\vec{r}_j - \vec{r}_i|$ of separation of the j th and i th particles, $U(\vec{r}_j, \vec{r}_i) = U(r)$. Particles are assumed spherical so that no orientation effects enter and we take that the potential energy between a pair of adsorbed molecules is given by

$$U(r) = \begin{cases} +\infty & \text{for } r < \sigma \\ -U_0(T)(\sigma/r)^6 & \text{for } r \geq \sigma, \end{cases} \quad (9)$$

i.e. we use the "hard-sphere" core and the usual r^{-6} attractive term for large r ; the minimum occurs at $r = \sigma$ for which $U(r = \sigma) = -U_0(T)$. The argument (T) in the parameter $U_0(T)$, $U_0(T) \geq 0$, signifies that in general case, this property can be dependent on the temperature. Particularly, for the Keesom-van der Waals interactions one has $U_0(T) \sim 1/T$. For the London-van der Waals particle-particle interactions $U_0(T)$ does not vary with the temperature. As we have already mentioned, we will suppose in what follows that the amplitude of the particle-particle attraction $U_0(T)$ is less than the barrier for the lateral motion, i.e. V_l , such that the particle-particle interactions do not perturb significantly the array of potential wells created by the particle-solid interactions.

Now, we specify the particle dynamics more precisely (see also [26, 27]). Under the physical conditions as described above, we can regard the particles dynamics on the solid surface as an activated

hopping between the local minima of an array of potential wells, created due to the SP interactions [41, 42]. Thus particles' migration on the surface proceeds by rare events of hopping from one well to another in its neighborhood. The hopping events are separated by the time interval τ , which is the time a given particle typically spends in each well vibrating around its minimum; τ is related to the temperature $T = \beta^{-1}$, the barrier for lateral motion V_l and the frequency of solid atoms vibrations ω through the Arrhenius formula. We thus may estimate the diffusion coefficient for such a motion (which will be exactly the diffusion coefficient of an isolated particle on the solid surface) as $D_0 \approx l^2/z\tau$, where z is the coordination number of the lattice of wells and l is the interwell spacing. In what follows we will suppose that $l \approx \sigma$, i.e. that the radius of the particle-particle hard-core and the interwell spacing are approximately the same. Now, diffusion coefficient D_0 will be the only pertinent parameter describing the evolution of the local density in the monolayer in absence of the PP interactions. When the latter are present, as we actually suppose here, dynamics of any given particle is fairly more complicated and is coupled to the instantaneous configuration of the monolayer particles (see, e.g. [50, 51, 52, 53] for discussion). That is, for any particle, releasing from the well with radius-vector \vec{r} , not all hopping directions are equally probable and the particle has a tendency to follow the local gradient of the energetic surface $U(\vec{r}; t)$, created by the mutual PP attractions. On the other hand, hard-core repulsion imposes sterical constraints preventing particles crossing and thus the double occupancy of any potential well. More specifically, we will account for the PP interactions as follows: we will suppose that releasing at time moment t from the well with radius-vector \vec{r} any given particle first "chooses" the direction of jump with the (position- and time-dependent) probability

$$p(\vec{r}|\vec{r}') = Z^{-1} \exp\left(\frac{\beta}{2} [U(\vec{r}; t) - U(\vec{r}'; t)]\right), \quad (10)$$

where \vec{r}' is the radius-vector of one of z wells neighboring to the well at position \vec{r} , Z is the normalization factor, defined as

$$Z = \sum_{\vec{r}'} \exp\left(\frac{\beta}{2} [U(\vec{r}; t) - U(\vec{r}'; t)]\right), \quad (11)$$

in which the sum runs over all wells neighboring to the well as position \vec{r} , and the PP energy landscape is determined by

$$U(\vec{r}; t) = -U_0(T) \sigma^6 \sum_{\vec{r}''} \frac{\eta(\vec{r}''; t)}{|\vec{r} - \vec{r}''|^6} \quad (12)$$

In the latter equation the summation with respect to \vec{r}'' extends over the entire surface, excluding $\vec{r}'' = \vec{r}$, and $\eta(\vec{r}''; t)$ is the time-dependent occupation variable of the well at position \vec{r}'' at time t ; $\eta(\vec{r}''; t) = 1$ if the well is occupied by a monolayer particle and $\eta(\vec{r}''; t) = 0$ if it is empty.

Finally, hard-core part of the interaction potential in Eq.(9) will be taken into account in the following way: we suppose that when the jump direction is chosen, the particle attempts to jump into the target well. We stipulate, however, that the jump can be only then fulfilled, when at this time moment the target well is empty; otherwise, the particle attempting this hop is repelled back to its position.

In such a picture of particles dynamics and interactions, which represents, in fact, the standard formulation of a hard-core lattice gas dynamics under long-range particle interactions, the evolution of the local occupation variable $\eta(\vec{r}; t)$ can be described by an appropriate probabilistic generator $L\{\eta(\vec{r}; t)\}$ (see, e.g. [51, 52]). Here we will not go into the details of rigorous probabilistic formulations, and will proceed by making a simplifying physical assumption that the realization average of the product of the local occupation variables of different wells factorize into the product of their average

values, which corresponds to the assumption of local equilibrium. It was shown recently in [54, 55] that such an assumption provides an adequate description of particles dynamics in hard-core lattice gases and we thus expect that it will be also a fair approximation for the system under study. The assumption of the local equilibrium allows us to describe the system evolution in terms of local densities $\rho(\vec{r}; t)$, $\rho(\vec{r}; t) = \overline{\eta(\vec{r}; t)}$, which define the probability of having at time t a particle in the well at position \vec{r} . Consequently, instead of the probabilistic equations describing evolution of $\eta(\vec{r}; t)$, we will have to consider a deterministic integro-differential equation describing evolution of the the local densities $\rho(\vec{r}; t)$. In doing so, we find then that the dynamics of $\rho(\vec{r}; t)$ is governed by the following continuous-time equation

$$\begin{aligned} \tau \frac{\partial \rho(\vec{r}; t)}{\partial t} = & - \rho(\vec{r}; t) \sum_{\vec{r}'} \overline{p(\vec{r}|\vec{r}')} (1 - \rho(\vec{r}'; t)) + \\ & + (1 - \rho(\vec{r}; t)) \sum_{\vec{r}'} \overline{p(\vec{r}'|\vec{r})} \rho(\vec{r}'; t), \end{aligned} \quad (13)$$

where the realization-average transition probabilities are given by

$$\overline{p(\vec{r}|\vec{r}')} = Z^{-1} \exp \left(-\frac{\beta U_0(T) \sigma^6}{2} \left[\sum_{\vec{r}''} \frac{\rho(\vec{r}''; t)}{|\vec{r} - \vec{r}''|^6} - \sum_{\vec{r}''} \frac{\rho(\vec{r}''; t)}{|\vec{r}' - \vec{r}''|^6} \right] \right) \quad (14)$$

Eq.(13) has a simple physical meaning - it describes the balance between the departures of a particle from the well at position \vec{r} to any of the neighboring wells and the arrivals of particles from the neighboring wells to the well at position \vec{r} . Particularly, the first term on the right-hand-side of Eq.(13) describes all possible events in which a particle, occupying at time t the well at \vec{r} (the factor $\rho(\vec{r}; t)$) may jump, at a rate $p(\vec{r}|\vec{r}')$ prescribed by the corresponding change in the energy of the monolayer, to any of vacant (the factor $(1 - \rho(\vec{r}'; t))$) adjacent wells. In a similar fashion, the second term describes the corresponding (positive) contribution due to arrivals of particles from adjacent wells to the well at position \vec{r} .

Eq.(13) has to be solved subject to the initial condition

$$\rho(\vec{r}; 0) = \begin{cases} 0 & \text{for } X > 0 \\ \rho & \text{for } X \leq 0, \end{cases} \quad (15)$$

where ρ denotes the initial mean coverage (number of occupied wells per total number of wells in a unit area) of the half-plane $X \leq 0$. Eqs.(13) and (15) represent the mathematical formulation of the problem under study and allow for the computation of the monolayer edge time evolution.

4 Approximations.

One possible approach is to seek for an approximate solution of Eqs.(13) and (15), turning to the continuous-space limit and expanding the local densities into the Taylor series up to the second order in powers of σ and the exponentials in Eq.(14) up to the first order in the gradient terms. In doing so, we obtain from our Eq.(13) the following continuous-space Fokker-Planck-type equation with non-local, configuration-dependent potential term

$$\begin{aligned} \frac{\partial \rho(\vec{r}; t)}{\partial t} = & D_0 [\Delta \rho(\vec{r}; t) - \beta U_0(T) \nabla \{ \rho(\vec{r}; t) \times \\ & \times (1 - \rho(\vec{r}; t)) \int d\vec{r}' \rho(\vec{r}'; t) \nabla \frac{1}{|\vec{r} - \vec{r}'|^6} \}] \end{aligned} \quad (16)$$

Equation (16), which was rigorously derived by Giacomini and Lebowitz [52] for related lattice-gas model with Kac potentials, allows for an analytic, although rather complicated analysis (see [52] for more details).

Here we will pursue, however, more simple approach of [26, 27], which allows for a quite straightforward computation of the mean displacement of the monolayer edge and of the edge tension directly from Eq.(13). Following [26, 27] we assume that for the long-range, but rapidly vanishing interaction potentials as defined in Eq.(9), a hop of any monolayer particle being in the "bulk" monolayer does not change the energy in Eq.(12). It means, in turn, that for such a particle all hopping direction appear to be equally probable and the hopping events are constrained by the hard-core interactions only. This is certainly not so for the particles being directly at the edge of the monolayer; these always have "free space" in front of them and the monolayer particles behind, which will result in effective attraction of the edge particles to the "bulk" monolayer and, in consequence, in asymmetric hopping probabilities: the edge particles will attempt preferentially to hop towards the "bulk" monolayer. In reality, all particles of the monolayer will experience a weak attraction in the negative X -direction. Being zero for $X = -\infty$, the effective attractive force will grow and reach its maximal value for $X = X(t)$, i.e. for the edge particles. Simplifying the actual picture to some extent, we will suppose here that this "restoring" force is present only for the particles which are directly at the edge (see also [26, 27]). This resembles, in a way, the model in [21, 22, 23], which was concerned with the dynamics of the edge due to the edge tension only. In contrast to this model, however, the approach of [26, 27] does not neglects the presence of the "bulk" monolayer phase; as we will see below the hard-core interactions between the particles in the "bulk" monolayer are crucially important and, particularly, are responsible for the \sqrt{t} -behavior in place of the linear in time dependence predicted by Eq.(7).

In a more precise way, the main assumptions of the approach in [26, 27] can be formulated as follows:

(a) Assume that at any time moment the monolayer is homogeneous in the direction normal to the X -axis. Consequently, the energy $U(\vec{r}; t)$ stays constant for any hop which does not change the particle position along the X -axis and the probability for such hops to take place is site-independent and is equal to $1/z$. This implies, in turn, that the edge of the monolayer is sharp (straight line) and allows to reduce the problem to the effectively one-dimensional model, in which the presence of the second direction is accounted for only through the renormalized diffusion coefficient and actual two-dimensional tension of the monolayer boundary.

(b) In the general case the monolayer edge will change its position along the X -axis, i.e. the monolayer will either contract or dilate in the X -direction, and thus the density will be dependent on the X -coordinate. One may suppose, however, that the density distribution $\rho(X; t)$ will be a slowly varying, at a microscopic scale, function of X , such that for weak long-range potentials in Eq.(9) and for X which are strictly less than the instantaneous position of the monolayer edge $X(t)$ the difference $U(X + \sigma; t) - U(X - \sigma; t) \ll 1/\beta$.

(c) Hopping probabilities of particles being directly at the edge obey Eq.(14) and thus depend implicitly on both $X(t)$ and $\rho(X; t)$. On the other hand, one may expect that after some transient period of time (which will be not studied here), the probability of making a jump away of the edge, i.e. $p(X(t)|X(t) + \sigma)$, and the probability of making a jump towards the "bulk" monolayer, i.e. $p(X(t)|X(t) - \sigma)$, approach some limiting values p and q , which do not depend on $X(t)$ and t . We note that this expectation is actually consistent with the solid-on-solid-model description of the liquid-vapour interface [21]. We will show below that this is actually the case and stems from the stabilization

of the density profile in the vicinity of the moving edge.

Finally, p and q are to be determined in a self-consistent way. To do this, we will first solve the model described by (a) - (c) supposing that p and q are known, fixed parameters, and calculate the time evolution of $X(t)$ and $\rho(X, t)$. Then, substituting the latter into Eq.(14), we will obtain the closed-form transcendental equation, which determines the dependence of p and q on $U_0(T)$, ρ and β .

5 Results.

Let us consider now the approximate picture of the monolayer evolution, described by (a) - (c), supposing first that p and q are some given parameters. We notice that such a picture has an evident interpretation within the framework of a lattice gas dynamics (Fig.3). It defines, namely, the evolution of a symmetric hard-core lattice gas, which is initially placed, at mean density ρ , at the sites $-\infty < X \leq 0$ of a one-dimensional infinite lattice of regular spacing σ . The particles are allowed to perform random hopping motion between the nearest-neighboring sites; the hopping motion is constrained by hard-core interactions. All particles, excluding the rightmost particle of the gas phase, have symmetric hopping probabilities, i.e. for them an attempt to hop to the right and an attempt to hop to the left occur with equal probability $m = 1/z\tau$. In contrast, for the rightmost particle these probabilities are asymmetric; they are equal to p and q for jumps away of and towards the gas phase respectively.

Dynamics of the rightmost particle in such an asymmetric, (with respect to the density distribution and the hopping probabilities of the rightmost particle), lattice-gas model has been analysed recently in [55]. It was shown that for arbitrary values of the ratio $\mu = p/q$, ($0 \leq \mu \leq 1$), the mean displacement of the rightmost particle follows

$$X(t) = A \sqrt{D_0 t}, \quad (17)$$

in which equation D_0 stands for the diffusion coefficient, $D_0 = \sigma^2/z\tau$, and the parameter A is determined implicitly as the solution of the transcendental equation

$$\frac{\sqrt{\pi} A}{2} \exp(A^2/4) [1 + \Phi(A/2)] = \frac{\mu - (1 - \rho)}{1 - \mu} \quad (18)$$

where $\Phi(x)$ denotes the probability integral. Besides, it was shown in [55] that at sufficiently large times the density distribution past the rightmost particle obeys

$$\rho(\lambda; t) = \frac{\rho}{1 + I(A)} \left\{ 1 + A^2 \int_0^\theta dz \exp\left(-\frac{A^2}{2}(z^2 - 2z)\right) \right\}, \quad (19)$$

in which

$$I(A) = \sqrt{\frac{\pi}{2}} A \exp(A^2/2) [1 + \Phi(A/\sqrt{2})], \quad (20)$$

and θ is the scaled variable, $\theta = \lambda/A\sqrt{D_0 t}$, where λ stands for the relative distance from the rightmost particle, $\lambda = X(t) - X$. In the limit $\lambda \ll \sqrt{D_0 t}/A$, Eq.(19) reduces to

$$\rho(\lambda; t) \approx (1 - \mu) \left[1 + \frac{A \lambda}{2\sqrt{D_0 t}} + \dots \right], \quad (21)$$

while in the opposite regime, when $\lambda \gg \sqrt{D_0 t}/A$, the density past the rightmost particle approaches the initial value ρ exponentially fast. It is important to notice that Eq.(21) shows that the density past the rightmost particle is almost constant (and different from ρ) in a certain region whose size grows

in proportion to $X(t)$. We note finally that for the just described one-dimensional model Eqs.(17) to (19) are exact, as it was shown subsequently by rigorous probabilistic analysis in [56].

Now, Eq.(18) predicts that four different regimes can take place, depending on the relation between μ and ρ . First, for $\mu < 1 - \rho$ the parameter A is negative and thus the rightmost particle effectively compresses the gas phase. When μ exactly equals $1 - \rho$, (which defines the "yield" value of μ necessary to initiate further compression), the prefactor A in Eq.(17) is exactly equal to zero, $A = 0$. Thus $X(t) = 0$ and the gas phase is stable. In this regime, however, despite the fact that $X(t) = 0$, the rightmost particle still wanders randomly around the equilibrium position and its mean-square displacement $X^2(t)$ grows with time. In [55] it was shown that the growth is sub-diffusive and $X^2(t) \sim (1 - \rho)t^{1/2}/\rho$. Further on, A is positive and finite when $1 < \mu < 1 - \rho$ holds; in this regime entropic effects overcome the pressure exerted by the rightmost particle and the gas slowly decompresses. Finally, when $\mu = 1$, the rhs of Eq.(18) diverges, which means that A is infinitely large in the steady-state. Actually, in this case A shows a slow, logarithmic growth with time. At sufficiently large times,

$$A \approx \sqrt{2 \ln\left(\frac{\rho^2 \omega t}{\pi}\right)} \quad (22)$$

Turning now back to the system under study, we have to identify μ and to express it through the strength of interactions $U_0(T)$, initial coverage ρ and the temperature β^{-1} . As we have already mentioned, the asymmetry in the hopping probabilities of the edge particles or, in other words, the "edge" tension force arises from the attraction of the edge particles to the "bulk" monolayer. Thus, since the interaction potential rapidly vanishes with the distance, we may expect that it is mostly dominated by the density profile in the vicinity of the moving edge, which is itself dependent on the magnitude of the edge tension. Self-consistent choice of μ is thus prescribed by Eq.(14), which relates the hopping probabilities p and q to the density profile in the monolayer. Taking into account the result in Eq.(21), which defines the density profile in the vicinity of the moving edge, we find from Eq.(14) that the ratio $\mu = p/q$ obeys

$$\mu = \exp(-\beta \sigma \gamma_{edge}) \quad (23)$$

In Eq.(23) the parameter γ_{edge} stands for the edge tension,

$$\gamma_{edge} = (1 - \mu) \frac{U_0(T) \delta}{2}, \quad (24)$$

and δ can be thought of as the number of broken cohesive bonds due to a hop away of the two-dimensional edge of the monolayer. Explicitly,

$$\delta = \sigma^5 \sum_{\vec{r}''} \left\{ \frac{1}{|\vec{r}_- - \vec{r}''|^6} - \frac{1}{|\vec{r}_+ - \vec{r}''|^6} \right\}, \quad (25)$$

where the shortenings \vec{r}_\pm stand for the vectors $(X(t) \pm \sigma, Y)$ and the sum extends over all lattice sites excluding $\vec{r}'' = \vec{r}_\pm$. For the simplest case of the square lattice, when $z = 4$, the parameter δ can be readily calculated in explicit form:

$$\delta = \sigma^{-1} \left[2 \sum_{j=1}^{\infty} j^{-6} + \sum_{j=-\infty}^{\infty} (1 + j^2)^{-3} \right] \approx 3.4 \sigma^{-1}, \quad (26)$$

which shows that in the presence of weak long-range attractive interactions δ only slightly exceeds $\delta_c = 3 \sigma^{-1}$ - the result which we would obtain in the extreme case of nearest-neighbor (Ising-type) attractions.

Therefore, we have that the mean displacement of the monolayer edge obeys Eq.(17), i.e. $X(t) = A\sqrt{D_0 t}$, which is consistent with the behavior predicted in [26, 27] for spreading ($A \geq 0$) precursor films. In our case of a semi-infinite monolayer, the parameter A in this growth law is defined implicitly through Eqs.(18), (24) and (25), which allow to interpret it in terms of the strength of the PP interactions, initial mean coverage ρ and the temperature. In Fig.4 we present numerical solution of these equations and plot A versus the dimensionless parameter $\epsilon = \beta U_0(T)\sigma\delta/2$, which appears to be the most significant critical parameter of the model. The solid curves in Fig.4 define the function $A(\epsilon)$ for four different initial densities. These curves demonstrate that the evolution of the monolayer is, in general, very sensitive to the value of ϵ and it may proceed rather differently, depending on the relation between this parameter and ρ .

We continue with some analytical estimates of the ϵ -dependence of the prefactor A , where we can specify four different regimes.

I. When ϵ belongs to a finite interval $0 \leq \epsilon \leq 1$ (high temperatures or low PP attraction), Eqs.(22) and (23) possess only one trivial solution $\mu = 1$, which means that in this range of parameters the "edge" tension is exactly equal to zero and the monolayer thus spreads as a surface gas. The edge in this regime advances a bit faster than pure \sqrt{t} -law and follows $X(t) \sim (t \ln(t))^{1/2}$. The particle density past the edge is almost zero within an extended interval, which grows in proportion to $X(t)$.

II. In the range $1 < \epsilon < \epsilon_c$, where

$$\epsilon_c = -\frac{\ln(1-\rho)}{\rho}, \quad (27)$$

the parameter A is finite and positive. Therefore, in this regime the monolayer also wets the substrate and the edge displaces in proportion to \sqrt{t} . It is easy to check that in this regime the edge tension γ_{edge} is positive and vanishes as

$$\gamma_{edge} \sim (T_b - T) \quad (28)$$

when the temperature T approaches the value T_b . The critical temperature T_b is implicitly defined by the condition $\epsilon = 1$, which can be rewritten as

$$T_b = \frac{U_0(T_b) \sigma \delta}{2} \quad (29)$$

Now, since the edge tension is positive below the T_b and is exactly zero above the T_b , it seems natural to identify this regime as the regime of liquid-like spreading and, correspondingly, the temperature T_b - as the temperature of the surface gas-liquid transition or, in other words, as the boiling temperature of the monolayer on solid surface. We note finally that the parameter A diverges in the limit $T \rightarrow T_b$, (when $\epsilon \rightarrow 1$),

$$A \sim \sqrt{\ln\left(\frac{\rho}{\epsilon-1}\right)} \quad (30)$$

Within the opposite limit $\epsilon \rightarrow \epsilon_c$, the parameter A vanishes as

$$A \sim \frac{(1-\rho)(\epsilon_c - \epsilon)}{1 - (1-\rho)\epsilon_c} \quad (31)$$

In this liquid-like spreading regime, the particle density past the edge is nearly constant within a region of size $X(t)$ and is lower than the unperturbed density ρ in the bulk monolayer.

III. At the point $\epsilon = \epsilon_c$ the monolayer partially wets the substrate; $\rho(\lambda; t) = \rho$ and the prefactor A is exactly zero. We thus denote this point as the point of the wetting/dewetting transition. The corresponding critical temperature $T_{w/dw}$ is defined by Eq.(27), which gives, explicitly,

$$T_{w/dw} = \frac{U_0(T_{w/dw}) \sigma \delta}{2\epsilon_c} \quad (32)$$

Thus, this critical temperature appears to depend on the monolayer coverage ρ . We note now that two critical temperatures are simply related to each other. When $U_0(T)$ is independent of T , like it is in the case of the London-van der Waals interactions, we find the following relation

$$T_{w/dw} = \frac{T_b}{\epsilon_c} \quad (33)$$

For the Keesom-van der Waals interactions, when $U_0(T) \sim 1/T$, we find instead of Eq.(33),

$$T_{w/dw} = \frac{T_b}{\sqrt{\epsilon_c}} \quad (34)$$

For the monolayer, the wetting/dewetting transition point $\epsilon_c \rightarrow \infty$ when $\rho \rightarrow 1$; consequently, the critical temperature of the wetting/dewetting transition $T_{w/dw} \rightarrow 0$ in this limit. Within the opposite limit, i.e. when $\rho \rightarrow 0$, $T_{w/dw} \rightarrow T_b$.

IV. Finally, for $\epsilon > \epsilon_c$, which corresponds to the limit of either low temperatures or strong particle-particle attractions, the parameter A is negative, $A < 0$, and thus the presence of a monolayer with a given coverage ρ on the solid surface is energetically non-favorable; consequently, it dewets from the substrate. The ϵ -dependence of the parameter A appears to be very weak in this regime (see Fig.4), which means that compressibility of the monolayer is very low, being strongly limited by the process of diffusive squeezing out of "voids" at progressively larger and larger scales. The density before the retracting edge is higher than the mean value ρ in an extended region which grows in proportion to $X(t)$ (an analog of the rim in the hydrodynamic dewetting [33, 34, 35, 36]).

We hasten to remark, however, that the predicted weak ϵ -dependence of the parameter A concerns only the situation in which thickening of the monolayer is not allowed and in which the particle motion can be viewed as an activated hopping motion between the wells created by the particle-solid interactions; particle-particle interactions are assumed to be small compared to the particle-solid interactions, such that they can be treated only as a small perturbation. For liquids in confined geometries, where the geometrical constraints themselves do not allow for the thickening of the monolayer, the process of squeezing of voids out of the "bulk" monolayer will be the only mechanism of the dewetting process. However, for sufficiently strong particle-particle attractions, comparable to the diffusive barrier V_l , our approximate description of particles dynamics is not justified; consideration of the edge tension as the only driving force will not be appropriate either.

For monolayers on open solid substrates, thickening of the monolayer by forming progressively higher and higher "towers" [32], represents an additional mechanism of the dewetting process, which may be, under certain conditions, more efficient than diffusive squeezing of voids. One can thus expect that for sufficiently strong particle-particle interactions the dewetting will be facilitated by thickening of the film, resulting in more pronounced ϵ -dependence of the parameter A . As found in [32], in this regime the mean displacement of the edge still follows the \sqrt{t} -dependence, which means that A remains finite in the limit $t \rightarrow \infty$. We may, however, only speculate about the ϵ -dependence of the parameter A for such a process, since such a possibility is not included into the model. We sketch in

Fig.4 a hypothetical behavior in this regime (the curve given by squares). Lastly, when $U_0(T)$ becomes comparable to the adsorption barrier U_d , one may expect transition to the hydrodynamic dewetting, when the monolayer tends to form a macroscopically large droplet. This regime was examined (starting from sufficiently thick initial films, however) in [33, 34, 35, 36] and it is known that the edge in this regime displaces at a constant velocity, which means that here A does not tend to a constant value as $t \rightarrow \infty$, but rather increases indefinitely as time evolves, $A \sim -t^{1/2}$. In Fig.4 we mark the transition from the monolayer-dewetting regime to the hydrodynamic dewetting regime by the line of crosses. We can not, of course, identify precisely the value of the parameter ϵ at which such a transition takes place; this calculation requires, again, elaboration of the model allowing for the thickening of the monolayer.

We finally comment that our results interpret the notion of the two-dimensional volatility, which is commonly used in experimental literature on spreading of molecularly thin films, in terms of the parameters of the particle-particle interactions, particle density and the temperature. It is precisely the relation between the value of the parameter ϵ , which is the measure of the particle-particle cohesive interactions, and the critical value ϵ_c , which shows whether having a monolayer on the solid substrate is energetically favorable or not. Consequently, we may expect that liquids with $\epsilon \geq \epsilon_c$ are not volatile in two dimensions, while liquids with $\epsilon < \epsilon_c$ are.

6 Conclusions.

To summarize, we have presented a microscopic dynamical description of the time evolution of a monolayer on solid surface. The monolayer was assumed to be created in initially non-equilibrium configuration, in which it covers only one half of the solid surface, and then was allowed to evolve in time due to particles random motion. Particles hopping motion was determined as the Kawasaki particle-void exchange dynamics in presence of long-range particle-particle attractions [52]. Here we have focused exclusively on a two-dimensional behavior, assuming that particle evaporation from the substrate is absent and thickening of the monolayer is forbidden. We have shown that in such a situation the behavior of the monolayer is very sensitive to physical conditions and parameters of the particle-particle attractions. Depending on the strength of the latter, the monolayer can show different kinetic behavior; it can wet, partially wet or spontaneously dewet from the substrate. More precisely, our results can be summarized as follows. We find that the mean displacement of the monolayer edge $X(t)$ evolves as $X(t) = A(D_0 t)^{1/2}$, where D_0 is the bare diffusion coefficient describing dynamics of an isolated particle on top of solid surface, while A is some parameter dependent on the strength of liquid-liquid attractions $U_0(T)$ and temperature T . At sufficiently high temperatures, such that $T \geq T_b$, the parameter A is greater than zero and shows a slow growth with time, $A \sim (\ln(t))^{1/2}$. We identify this regime as "surface-gas" spreading, since the tension of the monolayer edge appears to be equal to zero. Actually, in this regime the density past the edge is almost zero in an extended interval, whose size grows in proportion to $t^{1/2}$. Next, in the range of temperatures $T_b > T > T_{w/dw}$ the parameter A is also positive but tends to a certain constant value as $t \rightarrow \infty$. The edge tension in this regime is positive and we thus call it as the regime of "liquid-like" spreading. The density past the edge is constant within the interval of size $X(t)$ and is less than the density in the bulk monolayer. Thus in both regimes the monolayer expands and wets the substrate. Further on, at $T = T_{w/dw}$ the parameter $A = 0$, i.e. there is no regular dependence of the displacement of the edge on time and the monolayer remains in its initial configuration. Finally, below the temperature of the wetting-dewetting transition, $T_{w/dw}$, the parameter A is constant and negative, i.e. the monolayer contracts by squeezing out the "voids" and dewets from the solid surface.

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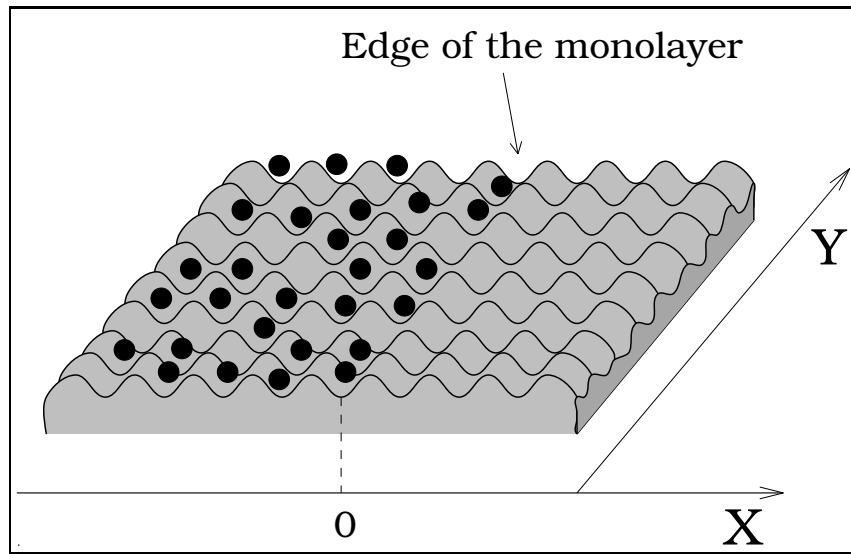


Fig.1. Initial configuration of a monolayer on top of solid surface. Wavy lines depict the potential energy landscape created by the solid atoms.

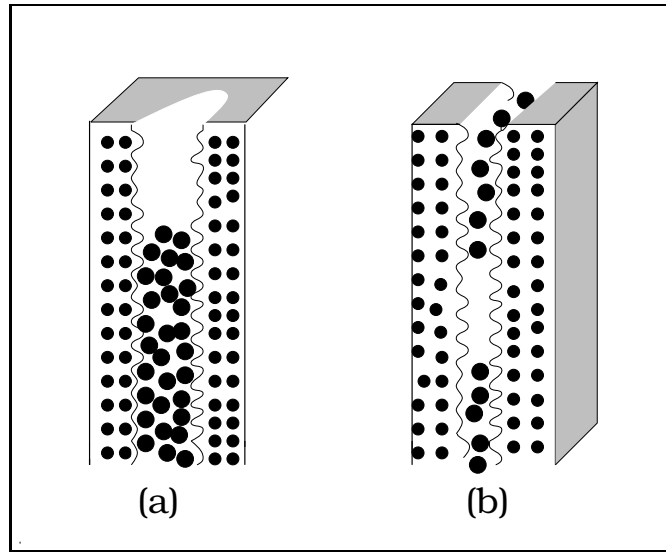


Fig.2. Liquids in confined geometries: (a) Uptake of liquid in a nanopore. (b) Ultrathin liquid film with a fluctuation-induced "hole", sandwiched in a microscopically thin slit between two macroscopically large solid surfaces.

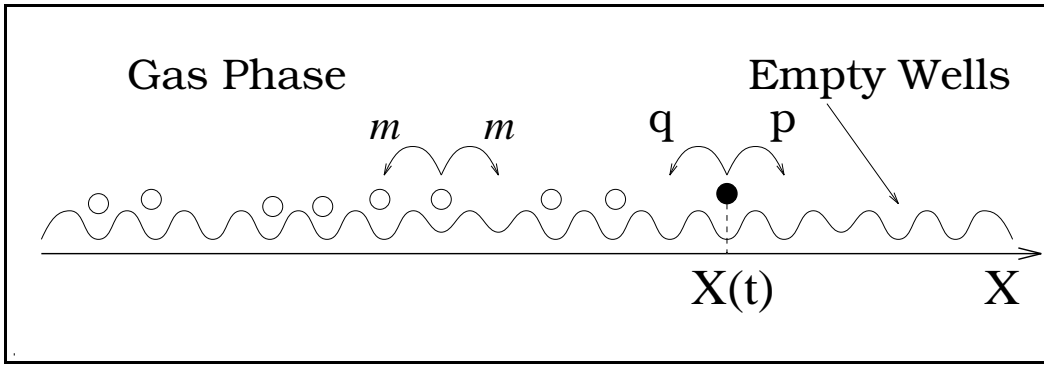


Fig.3. Associated one-dimensional hard-core lattice gas model. Empty circles denote the hard-core gas particles, whose probabilities m of jumps to the right and to the left are symmetric. The filled circle stands for the rightmost particles with asymmetric hopping probabilities, p and q .

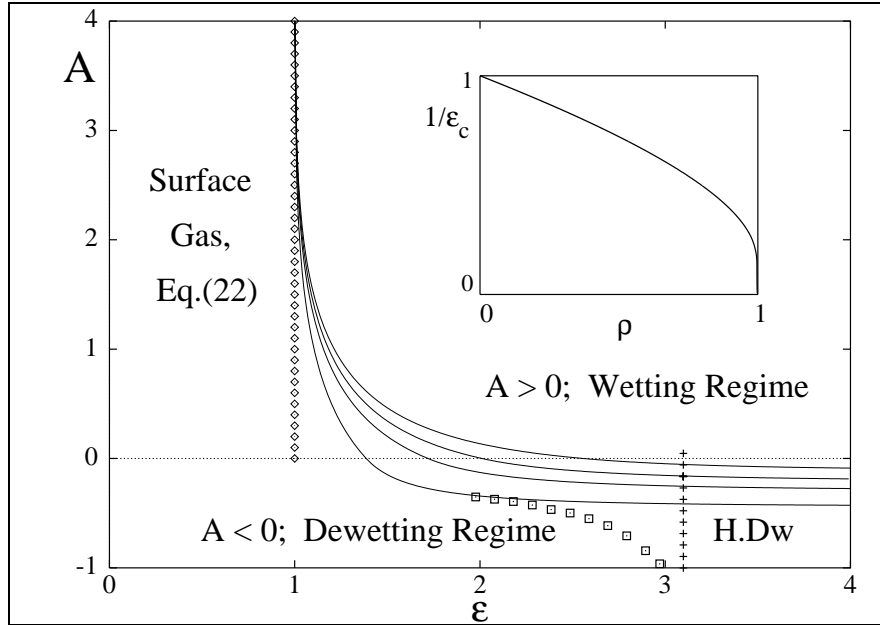


Fig.4. Numerical solution of Eqs.(18),(24) and (25). Solid lines from top to bottom show the dependence of the parameter A on ϵ for $\rho = 0.9, 0.8, 0.7$ and 0.5 respectively. The inset displays behavior of ϵ_c (the point in which the curve $A(\epsilon)$ crosses zero) as the function of the monolayer density ρ . Diamonds indicate the boundary line $\epsilon = 1$, which separates the "surface gas" and liquid-like behaviors. The crosses outline the demarcation line between the dewetting in the monolayer regime and the hydrodynamic dewetting (H.Dw), when thickening of the film can appear; the squares present the hypothetical continuation of the curve $A(\epsilon)$ in the hydrodynamic dewetting case (see also explanations in the text).